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# Synthesis and Luminescent Properties of Novel Platinum (II) Acetylide Complexes and Polymers with Toly Phosphine as Auxiliary Ligand

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**Abstract:** A new family of luminescent platinum acetylide complexes and polymer were formed by the Copper(I) catalyzed reaction of *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] (R= C<sub>6</sub>H<sub>5</sub>-*p*-CH<sub>3</sub>) with appropriate acetylide ligands. The reaction of metal precursors with 2.5 equivalents of acetylide ligands provided metal complexes *trans*-[Pt(*p*-tolyl<sub>3</sub>P)<sub>2</sub>(C≡C-R)<sub>2</sub>] (R= C<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>, C<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>), and equimolar amounts of ligand and metal precursor under refluxed condition provided metal poly-yne polymer [-Pt(*p*-tolyl<sub>3</sub>P)<sub>2</sub>C≡C-R-C≡C-]<sub>n</sub>, (R=biphenyl and 2,5-dioctyloxybenzene). Characterization of the newly developed polymer and metal complexes was accomplished by FT-IR, multinuclear NMR (<sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C), and mass spectrometry as well as elemental analysis. The molecular structure of the metal complexes was confirmed by single crystal X-ray crystallography. The photophysical properties such as electronic absorption and photoluminescence spectra of the metal complexes and polymer have been investigated. The studies reveal that the presence of heavy metal atom and substituent groups in the phenyl ring of the ligands can enhance the efficiency of intersystem crossing from the S<sub>1</sub> singlet excited state to the T<sub>1</sub> triplet excited state and thus give intense phosphorescence. The polymer is found to be non-emissive both at room temperature and low temperature.

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**Keywords:** Acetylide, Platinum, Polymer, X-ray, Phosphorescence

# 1 Introduction

The chemistry of transition metal acetylide complexes attracted a great interest in the last two decades due to their potential application in electronic industry. Especially  $\sigma$  bonded acetylide complexes and polymers of Pt, Pd, Ru and Ni have unique magnetic, electronic, liquid crystal, luminescence and nonlinear optical properties [1-9]. The photophysical properties of the metal containing conjugated polymers are dominated by prolonged phosphorescent  $\pi$ ,  $\pi^*$  excited states [10-20]. Because of their high triplet yield and relatively large triplet-singlet radiative decay rates, platinum-acetylide polymers are very useful for the development of optoelectronic devices such as organic light emitting diodes (OLED), photovoltaic cell, field effect transistors (FET) and non-linear optical system [21-29]. Transition metal acetylide complexes specially that of group 10 metals (Ni, Pd, Pt) of the type  $L_2Pt(C\equiv CR)_2$  [ $L = PMe_3, PEt_2, PBu, PPh_3, PmePh_2$  etc.  $R = H, CH_3, Ph, C_6H_5(OR)_2$ ] were first synthesized by Hagihara *et al.* by dehydrohalogenation [30, 31] or by ligand exchange reaction [32] using catalytic amount of CuI. Later several complexes and polyyne polymers have been synthesized and their photophysics were studied [33-44]. Some fundamental facts about the nature of singlet states were understood by thorough studies on the photophysics of conjugated organic polymers and monomers such as arylacetylenes, poly(arylethynynes)s. But relatively little is known about the triplet excited state [45-47]. It has been found from some recent study that the triplet state plays an important role in optical and electrical processes and is responsible for the ultimate efficiency of light emitting diodes (LEDs) [48-50]. The phosphorescence is rarely observed in conjugated organic molecules because the population of triplet excited state is very low. But interestingly, the presence of heavy transition metal in ethynyl complexes and in conjugated polyyne polymers can mix the singlet and triplet excited states *via* strong spin orbit coupling, rendering the triplet emission (phosphorescence) partially allowed [51-56].

In the frame of previous work in this field of chemistry, we therefore study herein the synthesis, characterization, solution absorption and photoluminescence spectra of some platinum acetylide complexes and poly-yne polymers and hence enrich this family of novel compounds.

## 2 Experimental

### 2.1 Materials and measurements

Solvents were dried with appropriate drying agent ( $\text{CH}_2\text{Cl}_2$  and  $\text{Et}_2\text{NH}$  by refluxing with KOH pellets for 20 hours), and degassed by nitrogen bubbling before use. All chemicals, unless otherwise mentioned, were obtained from commercial sources and used as received. The starting complex *cis*- $[\text{PtCl}_2(p\text{-tolyl}_3\text{P})_2]$  and ligands 4,4-bis-ethynyl biphenyl, 1,4-diethynyl-2,5-bis(octyloxy) benzene and *p*-nitrophenylacetylene were prepared according to the literature methods [57,58]. All reactions were performed strictly under nitrogen atmosphere using standard technique. Preparative TLC was performed on silica plates obtained from Macherey-Nagel, Germany. Infrared spectra were recorded in Shimadzu FTIR using KBr (for solid) and dry  $\text{CH}_2\text{Cl}_2$  (for liquid) as background, NMR were measured in  $\text{CDCl}_3$  on a BRUKER (400 MHz) NMR spectrophotometer. The chemical shifts were referenced to TMS for  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and trimethylphosphite for  $^{31}\text{P}$ -NMR spectra. ESI mass spectra were recorded on Brucker Daltonics Esquire-LC mass spectrophotometer. Electronic absorption spectra were obtained with a Hewlett-Packard 8453 UV-vis spectrometer. For emission spectral measurement, the 325 nm line of a He-Cd laser was used as an excitation source. The luminescence spectra were analyzed by a 0.25 m focal length double monochromator with a Peltier cooled photomultiplier tube and processed with a lock in amplifier. For low temperature measurements, sample were mounted in a closed-cycle cryostat (Oxford CC1104) in which the temperature can be adjusted from 10 to 330 K. The molecular weights of the polymer were determined by GPC (HP 1050 series HPLC with visible wavelength and fluorescent detectors) on the basis of a polystyrene calibration and

thermal analyses were performed under nitrogen with a Perkin TGA6 thermal analyzer at a heating rate of 20°C/min.

### ***Method of Single crystal X-ray Crystallography***

## **2.2 Synthetic Procedure**

### ***2.2.1 Trans-di (p-nitrophenylacetylide)bis(tri-p-tolylphosphineplatinum(II)), 1***

To a solution of *cis*-[PtCl<sub>2</sub>(*p*-tolyl<sub>3</sub>P)<sub>2</sub>] (0.200 g, 0.228 mmol) in freshly dried and degassed diethyl amine (70 ml) were added *p*-nitrophenylacetylene (0.084 g, 0.57 mmol) and copper(I) iodide (0.002 g, 0.01 mmol) with a positive flow of nitrogen. The reaction mixture was allowed to stir at room temperature for 4 hours under strictly maintained inert atmosphere of nitrogen. The completion of the reaction was confirmed by IR spectrum and TLC analysis. The solvent was removed and the crude product was purified by column chromatography using neutral alumina (mesh 70-230) as stationary phase and a mixture of CH<sub>2</sub>Cl<sub>2</sub>/n-hexane at 2:1 ratios as mobile phase. After removal of solvent, pure pale yellow compound was obtained in 48% yield (0.502 g). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2012 cm<sup>-1</sup> (C≡C), 513 cm<sup>-1</sup> (Pt-C). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 2.36 (s, 18H, CH<sub>3</sub>), 6.28 (d, 4H, ArH), 7.15 (d, 12H, ArH), 7.63 (dd, 12H, ArH), 7.77 (d, 4H, ArH). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 144.16, 122.78, 131.08, 135.79 (Ar-NO<sub>2</sub>), 100.72, 112.90 (C≡C), 127.69, 134.9, 128.62, 140.65, 21.42 (Ar-CH<sub>3</sub>). <sup>13</sup>C-NMR (DEPT, δppm) 21.45 (-CH<sub>3</sub>), 122.8 (=CH<sub>2</sub>), 131.1 (=CH<sub>2</sub>), 134.8 (=CH<sub>2</sub>), 128.6 (=CH<sub>2</sub>). <sup>31</sup>P-NMR (CDCl<sub>3</sub>, 161 MHz) δ (ppm): 18.45 (<sup>1</sup>J<sub>Pt-P</sub> = 2561.50 Hz). ESI-MS: *m/z*=1118 (M + Na)<sup>+</sup>. Calc for C<sub>58</sub>H<sub>50</sub>O<sub>4</sub>N<sub>2</sub>P<sub>2</sub>Pt: C 63.56, H 4.60, N 2.56, Found: C 63.29, H 4.70, N 2.49 %.

### ***2.2.2 Trans-di(p-tolylacetylide)bis(tri-p-tolylphosphineplatinum(II)), 2***

The complex **2** was synthesized using similar procedures as described above for **1**, but *p*-tolylacetylene ligand was used instead of *p*-nitrophenylacetylene. The crude product was purified by column chromatography using neutral alumina (mesh 70-230) as stationary phase and a mixture of CH<sub>2</sub>Cl<sub>2</sub>/n-hexane at 4:3 ratios as a mobile phase. After evaporation of the solvent, deep yellow compound **2** was obtained in 85% yield (0.502 g).

IR (CH<sub>2</sub>Cl<sub>2</sub>): 2106 cm<sup>-1</sup> (C≡C), 522 cm<sup>-1</sup> (Pt-C). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, δ ppm): 2.36 (s, 18H, CH<sub>3</sub>), 2.17 (s, 6H, CH<sub>3</sub>), 6.15 (d, 4H, ArH), 6.71 (d, 4H, ArH), 7.13 (d, 12H, ArH), 7.70 (dd, 12H, ArH). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz, δppm ) 21.38, 142.05, 130.88, 127.70, 125.39, 110.4, 112.64 (CH<sub>3</sub>-Ar-C≡C), 127.69, 134.9, 128.6, 21.19 (Ar-CH<sub>3</sub>). <sup>13</sup>C-NMR (DEPT, δ ppm) 21.42 (-CH<sub>3</sub>), 130.92 (=CH<sub>2</sub>), 127.69 (=CH<sub>2</sub>), 135.06 (=CH<sub>2</sub>), 128.42 (=CH<sub>2</sub>), 21.19 (-CH<sub>3</sub>). <sup>31</sup>P-NMR (CDCl<sub>3</sub>, 161 MHz, δppm) 18.29 (<sup>1</sup>J<sub>Pt-P</sub>= 2631.51 Hz). ESI-MS: *m/z* = 1056 (M + Na)<sup>+</sup>. Calc for C<sub>60</sub>H<sub>56</sub>P<sub>2</sub>Pt: C 69.69, H 5.46, Found: C 69.58, H 5.40 %.

### 2.2.3 Polymer 3

A mixture of *cis*-[PtCl<sub>2</sub>(*p*-tolyl<sub>3</sub>P)<sub>2</sub>] (0.05 gm, 0.057mmol), 4,4'-bis-ethynylbiphenyl (0.012 gm, 0.057 mmol) and CuI (1 mg) in dried and degassed diethyl amine (60 ml) was refluxed and stirred for 5 hours in an inert atmosphere of nitrogen. The completion of the reaction was confirmed by IR spectra (no ≡C-H at ≈3300 cm<sup>-1</sup>). After removal of solvent, the crude product was purified by re-crystallization technique using dichloromethane and methanol to obtain **3** in 40% yield (0.023 gm). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2100 cm<sup>-1</sup> (C≡C), 520 cm<sup>-1</sup> (Pt-C), 3018 cm<sup>-1</sup> (Ar-H), 2862 cm<sup>-1</sup> (-C-H) 1597 and 1485 cm<sup>-1</sup> (Aromatic C=C). The solubility of **3** was too for recording NMR spectrum, and GPC.

### 2.2.4 Polymer 4

Similar procedure as discussed above for polymer **3** was followed to prepare polymer **4** using 4-diethynyl-2, 5-bis(octyloxy)benzene (0.021 gm, 0.057 mmol) instead of 4,4'-bis-ethynylbiphenyl. The pure pale yellow colored product was obtained by re-crystallization using dichloromethane and n-hexane in 69.84% yield (0.044 gm). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2102 cm<sup>-1</sup> (C≡C), 515 cm<sup>-1</sup> (Pt-C). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 0.88 (s, 6H, CH<sub>3</sub>), 1.07 (m, 4H, CH<sub>2</sub>), 1.19 (m, 16H, CH<sub>2</sub>), 1.27 (m, 4H, CH<sub>2</sub>), 2.22 (s, 18H, CH<sub>3</sub>), 3.19 (s, 4H, CH<sub>3</sub>), 6.99 (d, 12H, ArH), 7.07 (s, 2H, ArH), 7.62 (s, 12H, ArH). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm ): 21.38, 128.12, 135.22, 128.86, 139.52 (Ar-CH<sub>3</sub>), 112.15, 103.36, 144.52, 118.69, 152.33 (C≡C-Ar), 69.62, 31.99, 29.40, 25.96, 22.75, 14.19 (Octyloxy chain). <sup>13</sup>C-

NMR (DEPT)  $\delta$  (ppm): 21.40 (-CH<sub>3</sub>), 135.22 (=CH<sub>2</sub>), 128.70 (=CH<sub>2</sub>), 118.64 (=CH<sub>2</sub>), 69.62 (-CH<sub>2</sub>), 32.05 (-CH<sub>2</sub>), 29.4(-CH<sub>2</sub>), 22.75 (-CH<sub>2</sub>), 14.19 (-CH<sub>2</sub>). <sup>31</sup>P-NMR (CDCl<sub>3</sub>, 161 MHz)  $\delta$  (ppm): 16.74 (<sup>1</sup>J<sub>Pt-P</sub> = 2663.23 Hz), 20.64 (<sup>1</sup>J<sub>Pt-P</sub> = 2648.36 Hz).

## 3 Results and Discussion

### 3.1 Synthetic Studies

The synthesis of platinum acetylide complexes is outlined in path A of Scheme 1. The dehydrohalogenation method developed by Sonogashira and Hagihara *et al* [30-32] was employed for the synthesis of symmetrical bis-acetylide complexes. The reaction between acetylide ligand HC≡C-R (R= C<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>, C<sub>6</sub>H<sub>4</sub> -*p*-CH<sub>3</sub>,) and *cis*-[PtCl<sub>2</sub>(*p*-tolyl<sub>3</sub>P)<sub>2</sub>] for 2.5 hours, in diethyl amine, at room temperature, under strict nitrogen atmosphere, in presence of catalytic amount of CuI afforded the formation of *trans*-[Pt(*p*-tolyl<sub>3</sub>)<sub>2</sub>(C≡C-R)<sub>2</sub>] (R= C<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub> **1**, C<sub>6</sub>H<sub>4</sub> -*p*-CH<sub>3</sub> **2**) complexes. After purification by column chromatography using neutral alumina as stationary phase and CH<sub>2</sub>Cl<sub>2</sub>/n-hexane as mobile phase, pure compounds were isolated in 50 - 80 % yield. Path B depicts the synthetic route of alkoxy ethynyl bridged platinum polymer. Polymerization was carried out by the treatment of *cis*-[PtCl<sub>2</sub>(*p*-tolyl<sub>3</sub>P)<sub>2</sub>] with diethynyl ligands, diethyl amine, in presence of CuI catalyst under refluxed condition, in nitrogen atmosphere. The polymers were purified and isolated from the crude product by repeated precipitation dichloromethane to hexane. The platinum acetylide complexes and polymers are soluble in common organic solvents except polymer **3**. All the products are air stable.



## 3.2 Characterization

### 3.2.1 Platinum Acetylide Complexes

Both **1** and **2** gave satisfactory spectroscopic data corresponding to their expected molecular structures. IR spectroscopy is a very effective tool to study the formation of new platinum acetylide complexes. During course of reaction, disappearance of the  $\equiv\text{C-H}$  stretching vibrations at  $\sim 3300\text{ cm}^{-1}$  and appearance of  $\text{M-C}\equiv\text{C}$  stretching vibrations at  $\sim 2100\text{ cm}^{-1}$  suggesting the formation of metal-alkyne bonds. Only one characteristic  $\nu$  ( $\text{C}\equiv\text{C}$ ) absorption bands were observed for both the complexes that confirmed the *trans* orientation of acetylene ligands around the platinum center [34]. The  $\nu$  ( $\text{C}\equiv\text{C}$ ) stretching frequency of the  $-\text{NO}_2$  substituted aryl acetylides is lower in wavenumber than that of tolyl species. This is due to the higher degree of electron delocalization when electron withdrawing  $\text{NO}_2$  occupies the *para* position of the aryl ring. In the  $^1\text{H-NMR}$  spectra of **1** and **2**, the singlet signals at  $\delta$  2.36 were observed for the methyl proton of the tolyl phosphine group. The peaks appeared in the range of  $\delta$  7.13 -  $\delta$  7.70 which we assign to the aromatic protons of the tolyl phosphine group. For the complex **1**, the two doublets appeared at  $\delta$  7.77 and  $\delta$  6.25 confirms the presence of aromatic protons of nitrophenylacetylene ligands. Complex **2** showed two sets of doublets at  $\delta$  6.15 and  $\delta$  6.71 and one singlet at  $\delta$  2.17 which confirms the presence of aromatic and methyl protons of tolylacetylene ligands. The  $^{31}\text{P-NMR}$  spectra contained singlet with the expected satellites due to coupling with  $^{195}\text{Pt}$  nuclei at  $\delta$  18.45 [ $J_{\text{Pt-P}} = 2561.5$ ] for complex **1** and  $\delta$  18.29 [ $J_{\text{Pt-P}} = 2631.51$ ] for complex **2**. The  $^1J_{\text{Pt-P}}$  value for both the complexes is typical of those for related *trans*  $\text{Pt-P}_2$  systems [56, 69].

The symmetrical nature of all complexes was evident from the NMR spectral pattern. The  $^{13}\text{C-NMR}$  spectral data featured the carbon skeleton of the complexes and the presence of different types of methyl and methyne groups were fully resolved by  $^{13}\text{C-NMR}$  (DEPT) spectra that support the expected structure of the complexes. The signals at  $\delta$  100.72,  $\delta$  112.90 for complex **1** and  $\delta$  110.4,  $\delta$  112.64 for complex **2** clearly indicated the presence of  $\text{C}\equiv\text{C}$  unit in both complexes. The aromatic region of the  $^{13}\text{C-NMR}$  spectra of **1** and **2**

showed precise information about the regiochemical structure of the complexes. There should have no methylene carbons in the complexes but in  $^{13}\text{C}$ -NMR (DEPT) spectra, some peaks were observed in down position that might be due to the trapped solvent. The molecular formula for the complexes were established by an intense molecular ion peak at  $m/z=1056$  ( $\text{M}+\text{Na}$ ) $^+$  for **1** and at  $m/z=1118$  ( $\text{M}+\text{Na}$ ) $^+$  for **2** observed in the ESI mass spectrum.

### X-ray Crystallography

*Please describe the molecular structure*

Single crystal of complex *trans*-[Pt(*p*-tolyl<sub>3</sub>P)<sub>2</sub>(C≡C-C<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>)<sub>2</sub>] **1**, suitable for X-ray diffraction analysis were grown by slow evaporation of dichloromethane-hexane solutions. The molecular structure of the complex **1** are shown in Fig. 2 and selected structural parameters are presented in Table 1

### 3.2.2 Platinum Acetylide Polymer

The polymer **3** was insoluble in common organic solvents and thus it was characterized only by IR spectroscopy. The acetylinic terminal  $\equiv\text{C-H}$  stretching frequency was observed at  $3298\text{ cm}^{-1}$  for the ligands of the type  $\text{H-C}\equiv\text{C-R-C}\equiv\text{C-H}$  which was absent in both **3** and **4** polymers. This disappearance of  $\equiv\text{C-H}$  stretching frequency indicates the formation of metal-carbon  $\sigma$  bond. The  $\text{C}\equiv\text{C}$  stretching frequency for 4,4'-bis-ethynylbiphenyl ligand was at  $2108\text{ cm}^{-1}$  which was shifted to  $2100\text{ cm}^{-1}$  in polymer **3** and the  $\text{C}\equiv\text{C}$  stretching frequency for 1,4-diethynyl-2,5-bis(octyloxy)benzene ligand was found at  $2106\text{ cm}^{-1}$  which was shifted to  $2102\text{ cm}^{-1}$  in polymer **4**. This shifting of stretching frequency to lower value indicates the metal to ligand or ligand to metal back donation that weakens the carbon-carbon triple bond. The  $^{31}\text{P}$ -NMR spectra allow us to confirm that the polymer **4** has *trans* geometry with respect to the Pt center. Two set of singlets (16.74 ppm and 20.64 ppm) associated with satellites indicate the formation of low molecular weight polymers. The singlet at 16.74 ppm arose from phosphines in the repeating platinum centres and that of 20.64 ppm arose from phosphines in the terminal

platinum unit.  $^{31}\text{P}$  NMR spectra allow us to confirm that the polymers have *trans* geometry with respect to the Pt center [56, 69].

In the  $^1\text{H}$ -NMR spectra of **4**, the proton signals arising from the aromatic and other organic groups were clearly located. The  $^{13}\text{C}$ -NMR and  $^{13}\text{C}$ -NMR (DEPT) spectral features of the polymer **4** agree with the structure shown in scheme 1. The  $^{13}\text{C}$ -NMR spectra showed precise information about the regiochemical structure of the main chain skeleton of the polymer. The  $^{13}\text{C}$  resonances due to alkynyl and alkyl groups were also clearly identified.

#### **Molecular weight determination of polymer 4**

The molecular weight of polymer **4** was estimated by GPC using polystyrene standards for the calibration and by  $^{31}\text{P}$  NMR spectroscopy. In Table 1, we reported the molecular weight, the molecular weight distribution, and the degree of polymerization of the polymer obtained. The table also contains the degree of polymerization as estimated by the  $^{31}\text{P}$ -NMR spectroscopy. It was determined by the ratio of the integration of the  $^{31}\text{P}$ -NMR signal of the internal vs. terminal phosphines bonded to the platinum centers. The ratio of the integral is approx 4.5 indicated nine repeating units and two terminal units are present in the polymers.

It is worth mentioning that the GPC method does not give absolute values of molecular weights but provides a measure of hydrodynamic volume. In fact, using randomly coiled polystyrene as calibration standard, the molecular weight of rigid-rod materials may be overestimated [59, 60]. For this reason, the determination of the chain length by integration of the NMR signals of the internal vs. external groups is considered as much more reliable. A comparison of the chain length obtained from either  $^{31}\text{P}$  NMR or GPC analysis of **4** showed the expected discrepancy. The GPC technique overestimated the molecular weights of **4** because the rigid rod shape of this molecule magnifies its hydrodynamic volume with respect to that of the polystyrene standard of analogous molecular weight.

### 3.3 Photophysical Properties

Photophysical investigations were carried out to explore the effect of substituent group and heavy metal atoms on the excited state properties of phenylacetylene ligands. It is found that the new polymer and metal complexes are soluble in organic solvents, and easily treatable. The absorption and photoluminescence spectra were measured in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature. Relevant photophysical data are summarized in Table 2.

It has been found from the previous studies that HOMO and LUMO orbitals of *trans*-platinum acetylide complexes containing phenylacetylene ligands of the type *trans*-[Pt(*p*-tolylP<sub>3</sub>)<sub>2</sub>(C≡C-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>] have  $\pi$  characters. Also HOMO orbitals of Pt acetylides arise from overlap between  $\pi$  system of alkynyl ligand and  $d_{xy}$  and  $d_{yz}$  orbitals of the platinum and the LUMO orbitals originate from overlap between  $\pi^*$  orbitals of ligands and  $6p_z$  metal orbital [61]. Thus, the strong absorption and photoluminescence peaks and bands observed for the platinum acetylide complex **1** and **2** can be attributed to the  $\pi$ - $\pi^*$  transitions originated from the acetylenic portions of the chain for each compound that are also mixed with slight contributions from the metal orbital (Fig. 5). The complex **2** exhibits a lowest energy absorption band at 352 nm and the complex **1** shows a red shifted absorbance at 404 nm in comparison with the complex **2**, suggesting that though the nitro group is electron withdrawing group but it can increase the  $\pi$  conjugation in the metal acetylide system more than methyl group via resonance. This phenomenon is also found in the *cis* platinum acetylide complexes reported earlier (Fig. 4) [34]. The polymer **4** shows lowest energy absorption band at higher wavelength (400 nm) relative to complex **2** indicating that  $\pi$ -conjugation is extended along the whole chain with a more extended singlet excited state in the Pt (II) polymer. But interestingly, the complex **1** absorbs at lower energy than the polymer suggesting that the NO<sub>2</sub> group can delocalize the  $\pi$  electrons more strongly *via* resonance (Fig. 4).

The PL spectra were measured at different temperature. In the dilute fluid solutions at 298 K, an intense emission peak was observed at 464 nm for complex **1**, which is due to intra-ligand ( $\pi\pi^*$ ) fluorescence (i.e.,  $S_1-S_0$ ). The complex **2** was found non-emissive at 298K. As the temperature was cooled to 77 K, no fluorescence band was observed but only the heavy metal enhanced ligand based phosphorescence band is found at 545 nm for complex **1** and at 447 nm for complex **2**. The assignment of triplet emission is supported by the large Stokes shift and structured emission in accordance with earlier work on *trans*-platinum acetylide complexes [61-68].

A substantial red shift is observed in the photoluminescence spectra of complex **1** as compared to the complex **2** that is also can be attributed to the increased delocalization of  $\pi$  electrons by nitro group via resonance. The platinum actylide polymer was non-emissive both at room temperature and low temperature. This phenomenon was sometimes observed in the previous studies in case of platinum acetylide oligomers [55].

## 4 Conclusions

The paper comprises the synthesis and structural characterization of new class of luminescent *trans*- platinum acetylide complexes and poly-yne polymers having similar structural basis. The nature of the excited state in these systems has been investigated through systematic ligand variation and its influence on excited state properties. In this context, two platinum acetylide complexes were synthesized and studied - one having electron withdrawing NO<sub>2</sub> substituent in the *para* position of phenylacetylene ligand while the other contains electron releasing CH<sub>3</sub> substituent. One solution processable polymer is also synthesized to compare the influence of long chain alkynyl moiety on the excited state properties. The study reveals that both the platinum acetylide complexes can exert heavy-atom effects in the enhancement of ISC rate and the presence of substituent in the phenyl acetylene ligands can remarkably influence the excited state properties. The polymer is found to be non-emissive.

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## References

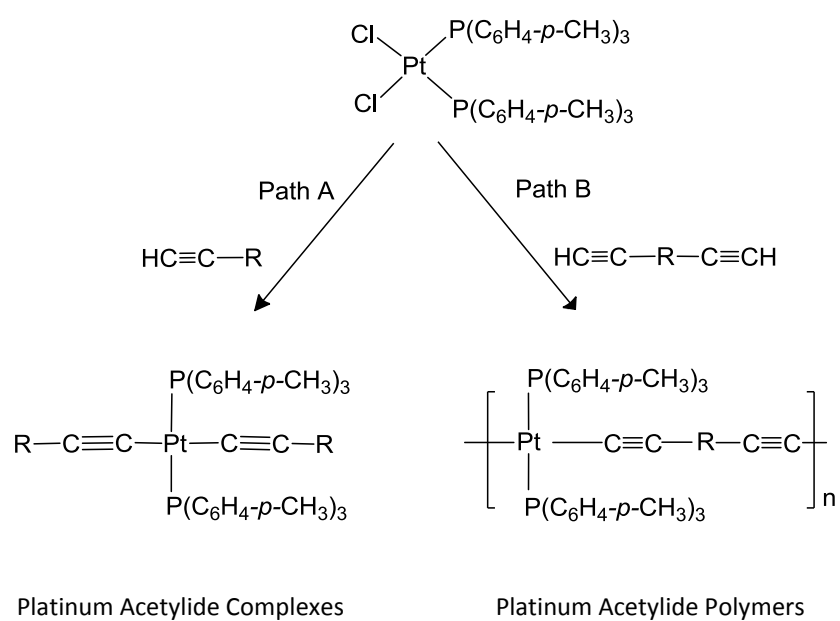
1. S. Riagaut, J. Perruchon, L. L. Pichon, D. Touchrad, P. H. Dixeneuf, *J. Organomet. Chem.*, **670** 37-44 (2003)
2. P. Nguyen, P. Gomez-Eliphe, and I. Manners, *Chem. Rev.* **99**, 1515 (1999)
3. Kokil, A.; Yao, P.; Weder, C. *Macromolecules* **124**, 9978 (2002)
4. Li Liu, Wai-Yeung Wong, Suk-Yue Poon, Kok-Wai Cheah, *J. Inorg. Organomet. Polym. Mater.* **15**, 555 (2005)
5. Wai-Yeung Wong, Yanhe Guo, Cheuk-Lam Ho, *J. Inorg. Organomet. Polym. Mater.* **19**, 46 (2009)
6. T. L. Stott, M. O. Wolf, *Coord. Chem. Rev.* **246**, 89 (2003)
7. M. Younus, N. J. Long, P.R. Raithby, J. Lewis, N. A. Page, A.J.P. White, D. J. Williams, M. C. B. Colbert, A. J. Hodge, M. S. Khan, D. G. Pagker, *J. Organomet. Chem.* **578**, 198 (1999)
8. F. Paul, C. Lapinte, *Coord. Chem. Rev.* **178-180**, 431 (1998)
9. Lewis, J.; Raithby, P. R.; Wong, W-Y.; *J. Organomet. Chem.*, **556** 219 (1998).

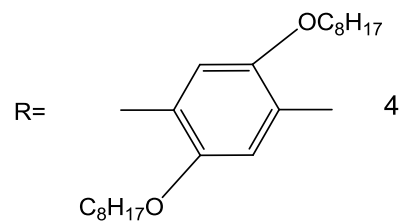
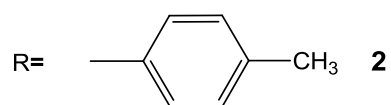
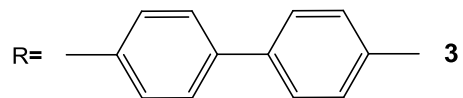
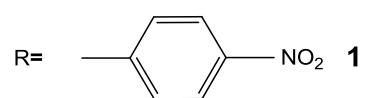
10. Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*, 2nd ed. (Marcel Dekker: New York, 1998)
11. McGehee, M. D. Miller, E. K.; Moses, D.; Heeger, A. J. *In Advances in Synthetic Metals. Twenty Years of Progress in Science and Technology*; Bernier, P. L., S., Bidan, G., Eds.; (Elsevier: Amsterdam, 1999), pp 98-205.
12. Wai-Yeung Wong, Suk-Yue Poon, Jian-Xin Shi, Kok-Wai Cheah, *J.Inorg. Organomet. Polym. Mater.* **17**, 189 (2007)
13. Kirk S. Schanze, Eric E. Silverman, and Xiaoming Zhao, *J. Phys. Chem. B* **109**, 18451(2005)
14. Beljonne, D.; Wittmann, H. F.; Köhler, A.; Graham, S. Y., M.; Lewis, J.; R., R. P.; Khan, M. S.; Friend, R. H.; Bredas, J. L. *J. Chem. Phys.* **105**, 3868 (1996)
15. K. A. Bunten, A. K. Kakkar, *Macromolecules*, **29**, 2885 (1996)
16. Chawdhury, N.; Köhler, A.; Friend, R. H.; Wong, W.-Y.; Lewis, J.; Younus, M.; Raithby, P. R.; Corcoran, T. C.; Al-Mandhary, M. R. A.; Khan, M. S. *J. Chem. Phys.* **110**, 4963 (1999)
17. GRogers, J. E.; Cooper, T. M.; Fleitz, P. A.; Glass, D. J.; McLean, D. G. *J. Phys. Chem. A* **106**, 10108 (2002)
18. Liu, Y.; Jiang, S.; Glusac, K.; Powell, D. H.; Anderson, D. F.; Schanze, K. S. *J. Am. Chem. Soc.* **124**, 12412 (2002)
19. Glusac, K.; Kose, M. E.; Jiang, H.; Schanze, K. S. *J. Phys. Chem.B* **111**, 929 (2007)
20. Wilson, J. S.; Köhler, A.; Friend, R. H.; Al-Suti, M. K.; Al-Mandhary, M. R. A.; Khan, M. S.; Raithby, P. R. *J. Chem. Phys.* **113**, 7627 (2000)
21. Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **105**, 1491 (2005)
22. Staromlynska, J.; McKay, T. J.; Bolger, J. A.; Davy, J. R. *J. Opt. Soc. Am. B* **15**, 1731 (1998)
23. Kokil, A.; Shiyanovskaya, I.; Singer, K. D.; Weder, C. *J. Am. Chem.Soc.* **124**, 9978 (2002)
24. Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **38**, 1350 (1999)
25. Guo, F. Q.; Kim, Y. G.; Reynolds, J. R.; Schanze, K. S. *Chem. Commun.* 1887 (2006)
26. Wilson, J. S.; Dhoot, A. S.; Seeley, A. J. A. B.; Khan, M. S.; Köhler, A.; Friend, R. H. *Nature* **413**, 828 (2001)
27. Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.;Thompson, M. E.; Forrest, S. R. *Nature* **395**, 151 (1998)
28. A. L. Groia, A. Ricci, M. Bassetti, D. Masi, C. Bianchini, C. L. Sterzo, *J. Organomet. Chem.* **683**, 406 (2003)
29. Wang, X-Z; Ho, C-L; Yan, L; Chen, X; Chen, Xun; Cheung, K-Y, Wong W-Y, *J. Inorg. Organomet. Polym. Mater.* **20**, 478 (2010)
30. K. Sonogashira, T. Yatake, Y. Tohda, S. Takahashi, N. Hagihara, *J. Chem. Soc. Chem Comm.* 291 (1977)



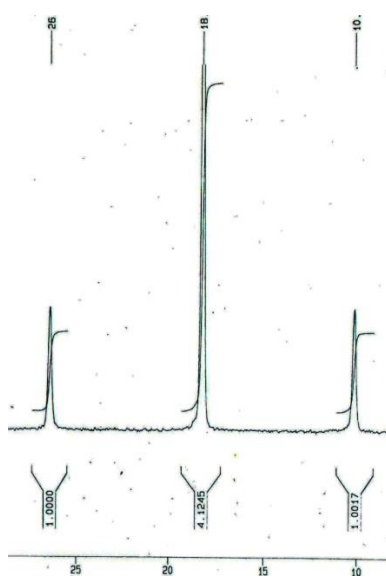
31. K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyashima, S. Takahashi, N. Hagihara, *J. Organomet. Chem.* **145**, 101 (1980)
32. K. Sonogashira, K. Ohga, S. Takahashi, N. Hagihara, *J. Organomet. Chem.* **188**, 237 (1980)
33. Kim, K.-Y.; Shelton, A. H.; Drobizhev, M.; Makarov, N.; Rebane, A.; Schanze, K. S. *J. Phys. Chem. A* **114** 7003 (2010)
34. Fengqi Guo, Wenfang Sun, Yao Liu and Kirk Schanze, *Inorg. Chem.* **44**, 4055 (2005)
35. Kye-Young Kim, Shengxia Liu, Muhammet E. Ko1se, and Kirk S. Schanze, *Inorg. Chem.* **45**, 2509 (2006)
36. M. V. Russo, C. L. Sterzo, P. Franceschini, G. Biagini, A. Furlani, *J. Organomet. Chem.* **619**, 49 (2001)
37. R. Saha, M. A. Qaium, D. Debnath, M. Younus, N. Chawdury, N. Sultana, G. Kociok-Kohn, P. R. Raithby, M. Kijima, *J. Chem. Soc. Dalton Trans.* 2760 (2005)
38. C. Huber, F. Bangerter, W. R. Caseri, C. Weder, *J. Am. Chem. Soc.* **123**, 3857 (2001)
39. N. J. Long, A. J. P. White, D. J. Williams, M. Younus, *J. Organomet. Chem.* **649**, 94 (2002).
40. M. S. Khan, S. J. Davies, A. K. Kakkar, D. Schwurtz, B. Lin, B. F. Johnson, J. Lewis, *J. Organomet. Chem.* **424**, 87 (1992)
41. K Wittmann, H. F.; Friend, R. H.; Khan, M. S.; Lewis, J. *J. Chem. Phys.* **101**, 2693 (1994)
42. Chen Liao, James E. Yarnell, Ksenija D. Glusac, and Kirk S. Schanze, *J. Phys. Chem. B* **114**, 14763 (2010)
43. Thomas Cardolaccia, Alison M. Funston, M. Erkan Kose, Julia M. Keller, John R. Miller, and Kirk S. Schanze, *J. Phys. Chem. B* **111**, 10871 (2007)
44. Joy E. Rogers, Jonathan E. Slagle, Douglas M. Krein, Aaron R. Burke, Benjamin C. Hall, Albert Fratini, Daniel G. McLean, Paul A. Fleitz, Thomas M. Cooper, Mikhail Drobizhev, Nikolay S. Makarov, Aleksander Rebane, Kye-Young Kim, Richard Farley, and Kirk S. Schanze, *Inorg. Chem.* **46**, 6483 (2007)
45. Yanli Tang, Zhijun Zhou, Katsu Ogawa, Gabriel P. Lopez, Kirk S. Schanze, and David G. Whitten, *Langmuir* **25**, 21 (2009)
46. J. L. Bredas, J. Cornil and A. J. Heeger, *Adv. Mater.* **8**, 447 (1996)
47. N. S. Sariciftci, (Ed.), Primary Photoexcitations in Conjugated Polymers: Molecular Excitation vs Semiconductor Band Model (World Scientific, Singapore, 1997)
48. C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *J. Appl. Lett.* **77**, 904 (2000)
49. A. S. Dhoot and N. C. Greenham, *Adv. Mater.* **14**, 1834 (2002)
50. X. Gong, J. C. Ostrowski, G. C. Bazan, D. Moses, A.J. Heeger, M. S. Liu and A. K. Y. Jen, *Adv. Mater.* **15**, 45 (2003)
51. J. M. Lupton, A. Pogantsch, T. Piok, E. J. W. List, S. Patil, and U. Scherf, *Phys. Rev. Lett.* **89**, 167401 (2002)

52. J. S. Wilson, N. Chawdhury, M. R. A. Al-Mandhary, M. Younus, M. S. Khan, P. R. Raithby, A. Kohler and R. H. Friend, *J. Am. Chem. Soc.* **123**, 9412 (2001)
53. Richard T. Farley, Qinglin Zheng, John A. Gladysz, and Kirk S. Schanze, *Inorg. Chem.* **47**, 2955 (2008)
54. Xiaoming Zhao, Thomas Cardolaccia, Richard T. Farley, Khalil A. Abboud, and Kirk S. Schanze, *Inorg. Chem.* **44**, 2619 (2005)
55. Eric E. Silverman, Thomas Cardolaccia, Xiaoming Zhao, Kye-Young Kim, Ksenija Haskins-Glusac, Kirk S. Schanze, *Coordination Chemistry Reviews* **249**, 1491 (2005)
56. Wai-Yeung Wong, *J. Inorg. Organomet. Polym. Mater.* **15**, 197 (2005)
57. J. Chatt and R.G. Hayter, *J. Chem. Soc. Dalton Trans.* 896 (1961)
58. S.Takahashi, Y. Kuroyama, K. Sonogahara and N. Hagihara, *Synthesis* **8**, 627 (1980)
59. U.H.F Bunz, *Chem. Rev.* **100**, 1605 (2000)
60. I. Manners, *Synthetic Metal-containing polymers* (Wiley-VCH, Weinheim, Germany, 2004), Chap. 5
61. Sacksteder L., Baralt E., Degraff B.A., Lukehart C.M., Demas J.N. *Inorganic Chemistry*, **30**, 2468-2476 (1991)
62. H. Lang, A. del Vilar an G. Rheinwald, *J. Organomet. chem.* **587**, 284 (1999)
63. P.K.M. Sui, S. W. Lai, W. Lu, N. Zhu and C. M. Che, *Eur. J. Inorg. Chem.*, 2749 (2003)
64. Y. Kong, J. Lee, D. Song an S. Wong, *Dalton Trans.* 3493 (2003)
65. H. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte and R. Eisenberg, *Inorg. Chem.*, **39**, 447, (2000)
66. S. C. Chan, M. C. W. Chan, Y. Wong, C. M. Che, K. K. Cheung and N. Zhu, *Chem. Eur. J.* **7**, 4180 (2001)
67. Y. Y. Ng, C. M. Che and S. M. Peng. *New J. Chem.* **20**, 781 (1996)
68. C. E. Whittle, J. A. Weinstein, M. W. George and K. S. Schanze, *Inorg. Chem.* **40**, 4053 (2001)
69. J. Lewis, N. J. Long, P. R. Raithby, G. P. Shields, W.-Y. Wong, and M. Younus, *J. Chem. Soc., Dalton Trans.* 4283 (1997)

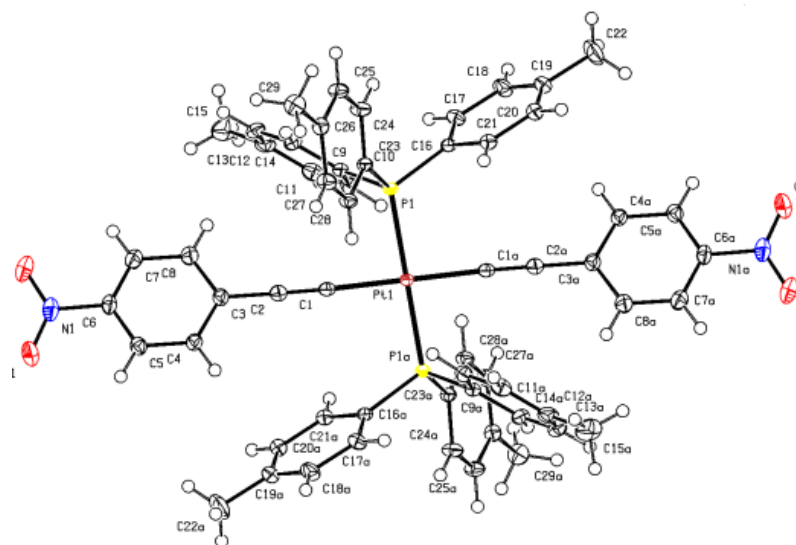




**Scheme 1**

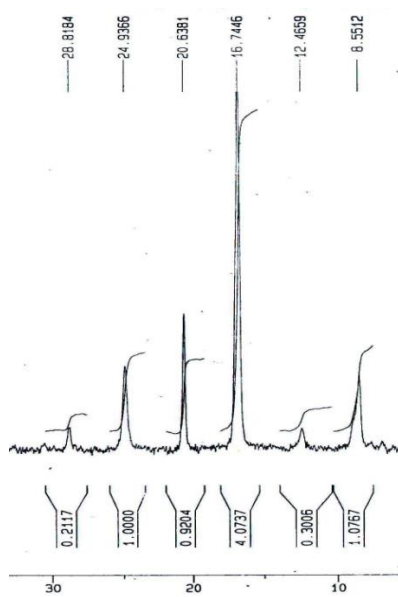


**Fig 1**



**Fig 2**

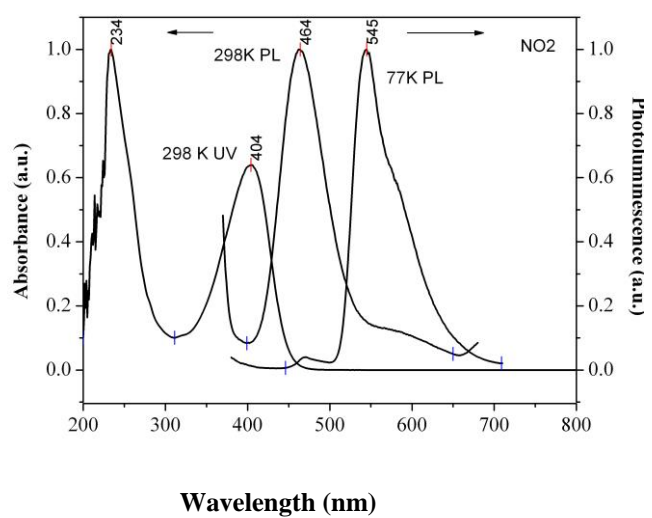




**Fig 3**

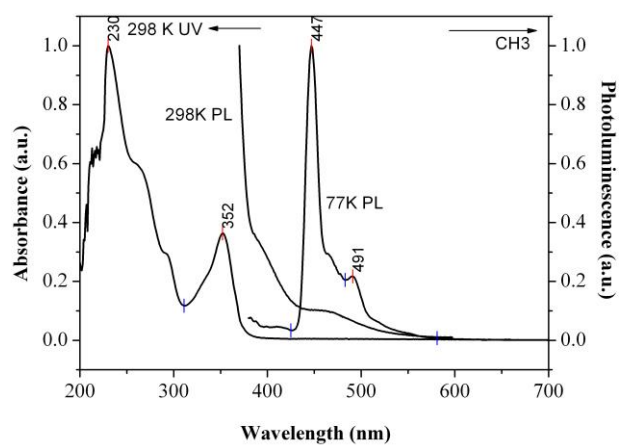


**Fig 4**

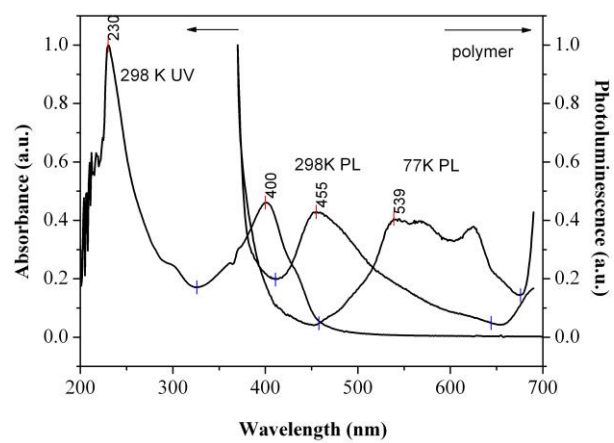


**1**





2



4

Fig 5

Table 1

Polymer	$M_n^a$	$M_w^b$	$M_w/M_n^c$	DP( $M_n$ )	DP( $M_w$ )	DP(NMR) <sup>f</sup>
4	14830	22780	1.54	13	19	9

<sup>a</sup>Number average molecular weight, <sup>b</sup>Weight-average molecular weight, <sup>c</sup>Molecular weight distribution, <sup>d</sup>Degree of polymerization calculated on the basis of  $M_n$  value, <sup>e</sup>Degree of polymerization calculated on the basis of  $M_w$  value, <sup>f</sup>Degree of polymerization calculated by <sup>31</sup>P NMR on the basis of terminal relative intensities of phosphorous signal

**Table 2**

<b>Material</b>	<b>Absorption at 298 K <math>\lambda_{\text{abs}}(\text{nm})</math></b>	<b>Emission (298 K) <math>\lambda_{\text{em}}(\text{nm})</math></b>	<b>Emission (77 K) <math>\lambda_{\text{em}}(\text{nm})</math></b>

<b>1</b>	234 400	464	545
<b>2</b>	230 352	----	447
<b>4</b>	230 400	455	539 625

### Figure Caption

Scheme 1: Synthesis of platinum acetylide complexes and polymers

Fig.1.  $^{31}\text{P}$ -NMR spectrum of platinum acetylide complex **2**

Fig. 2: The molecular structure of *trans*-[Pt(*p*-tolyl<sub>3</sub>P)<sub>2</sub>(C≡C-C<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>)<sub>2</sub>] **1**, showing the atom numbering scheme.

Fig. 3:  $^{31}\text{P}$ -NMR spectrum of Platinum Poly-yne polymer **4**

Fig 4:  $\pi$  conjugation in presence of NO<sub>2</sub> group in the metal acetylide system *via* resonance

Fig-5: The absorption and photoluminescence spectra of **1**, **2** and **4**

Table 1: Molecular weight for polymer **4**

Table 2: Photophysical data of platinum acetylide complexes and polymers